Statistical Thermodynamics in Chemistry and Biology

2. Extremum principles predict equilibria

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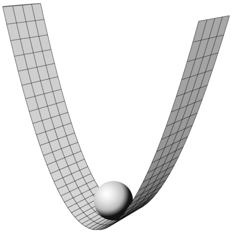
What are extremum principles?

- The *driving forces* on molecules are of two kinds:
  - The energy (in covalent bonds, intermolecular interactions) is minimized.
  - The entropy is maximized.
- Extremum (or variational) principles are obtained by minimizing or maximizing certain mathematical functions.

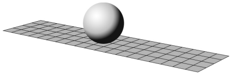
States of equilibrium - types of extrema (1)



- Stable equilibrium (at $x = x^*$):

$$V(x) - V(x^*) > 0 \quad \text{for all} \quad x \neq x^*$$

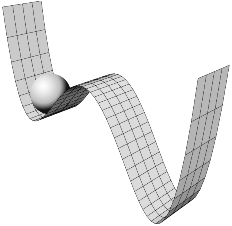
$$\frac{dV}{dx} = 0 \quad \text{and} \quad \frac{d^2V}{dx^2} > 0 \quad \text{at} \quad x = x^*$$



- Neutral equilibrium (at $x = x^*$):

$$\frac{dV}{dx} = 0 \quad \text{for all} \quad x$$

States of equilibrium - types of extrema (2)

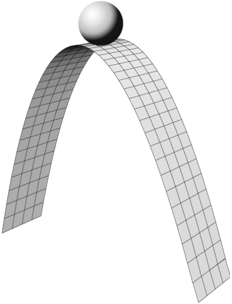


- Metastable equilibrium (at $x = x^*$):

$$V(x) - V(x^*) > 0 \quad \text{for small} \quad |x - x^*|$$

$$\frac{dV}{dx} = 0 \quad \text{and} \quad \frac{d^2V}{dx^2} > 0 \quad \text{at} \quad x = x^*$$

$$V(x) - V(x^*) < 0 \quad \text{for large} \quad |x - x^*|$$



- Unstable system (at $x = x^*$):

$$V(x) - V(x^*) < 0 \quad \text{for all} \quad x \neq x^*$$

$$\frac{dV}{dx} = 0 \quad \text{and} \quad \frac{d^2V}{dx^2} < 0 \quad \text{at} \quad x = x^*$$

An extremum principle for maximum multiplicity

Maximizing multiplicity predicts the highest probable outcome:

- Model system: 4 coin tosses
- Two of the possible outcomes: *HHHH* and *HTHH*
- Which sequence is most probable? *They are equally probable:* $\frac{1}{16}$
- Which composition is most probable? *4 of 16 sequences are composed by 3 H and 1 T; 1 of 16 sequences are composed by 4 H only*

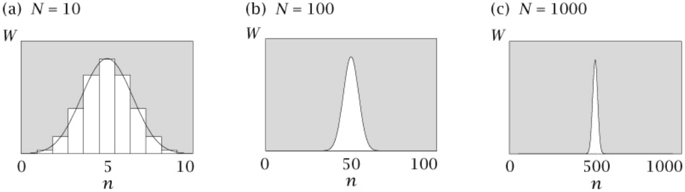
Maximizing multiplicity is equivalent to maximizing entropy.

Predicting heads and tails by a principle of maximum multiplicity

- N coin tosses; n heads; $(N-n)tails$
- The multiplicity, W, is given as

$$W(n,N) = \frac{N!}{\prod_i n_i!} = \frac{N!}{n!(N-n)!}$$

- Illustrated for $N=10$, $N=100$, $N=1000$.



- For large N, sharper and sharper peaks.
- Examples: $W(50,100) = 1.01 \times 10^{29}$ and $W(25,100) = 2.43 \times 10^{23}$
- For large N, we only need to consider $W^{\max}$

Stirling's approximation

Stirling's approximation[1] is common in statistical mechanics since factorials are often difficult to manipulate mathematically. It is valid for large N.

- Simpler approximation:

$$\ln N! \approx N \ln N - N \qquad \Rightarrow \qquad N! \approx \left(\frac{N}{e}\right)^N$$

- Better (less common) approximation:

$$\ln N! \approx \frac{1}{2}\ln 2\pi + \left(N + \frac{1}{2}\right)\ln N - N \qquad \Rightarrow \qquad N! \approx \sqrt{2\pi N}\left(\frac{N}{e}\right)^N$$

Exercise: Test Stirling's approximation for
$N = 5, 10, 50, 100, 500, 1000, 10000, 10^5, 10^6, \ldots$.
Hint: For large N for the "exact" calculation use

$$\ln N! = \sum_{m=1}^{N} \ln m$$

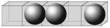
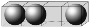
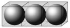
[1] See Appendix B

Results for exercise: Stirling's approximation

N	$\ln N!$	$N \ln N - N$	$\frac{1}{2}\ln 2\pi + \left(N + \frac{1}{2}\right)\ln N - N$
5	4.7875	3.0472	4.7708
10	15.1044	13.0259	15.0961
50	148.4778	145.6012	148.4761
100	363.7394	360.5170	363.7385
500	2611.3305	2607.3040	2611.3303
1000	5912.1282	5907.7553	5912.1281
10000	82108.9278	82103.4037	82108.9278
100000	1051299.2219	1051292.5465	1051299.2219
1000000	12815518.3847	12815510.5580	12815518.3847

- $\frac{1}{2}\ln 2\pi = 0.9189$

Lattice model for particles and “pressure”

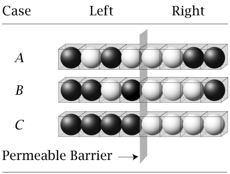
Case	Configuration	Volume
A		5
B		4
C		3

- $N = 3$ spherical particles
- Three different “volumes”: $M_A = 5$, $M_B = 4$, $M_C = 3$
- What value of M maximizes the multiplicity?
- Or what happens if the volume is suddenly expanded?
- Analogous to coin tossing: [*occupied, vacant, vacant, ...*]
- Multiplicity obtained as

$$W(N, M) = \frac{M!}{N!(M - N)!}$$

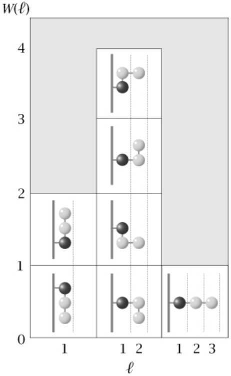
- $W_A(3, 5) = 10$, $W_B(3, 4) = 4$, $W_C(3, 3) = 1$
- The particles will be “fully spread out”

Lattice model for diffusion and mixing



- Four black particles and four white particles
- The total volume is fixed
- What is the most probable composition?
- $W = W_{\mathrm{left}} \cdot W_{\mathrm{right}}$
- $W_A = \frac{4!}{2!2!}\frac{4!}{2!2!} = 36,\ W_B = \frac{4!}{1!3!}\frac{4!}{3!1!} = 16,\ W_C = \frac{4!}{0!4!}\frac{4!}{4!0!} = 1$
- The driving force for getting the same “concentration” everywhere is named chemical potential

Lattice model for polymers



- Two-dimensional lattice model for a polymer with 3 monomers and connected to a wall.
- All the possible sequences are given in the figure.
- Which is the most probable composition, i.e. length of the polymer?

Summary

- We will use extremum principles. The (free) energy is minimized. The entropy is maximized.
- For large systems, only the maximum multiplicity is of importance. Then also Stirling's approximation may be used.
- The multiplicity of the system gives the entropy of the system, i.e. the multiplicity of the system is to be maximized.
- Considered three model systems: pressure, chemical potential, and polymer length.

Exercise E2.1

Consider N particles with a dipole moment placed on a quadratic lattice (surface). N is a large number so that the system can be regarded to be macroscopic. The dipole moment can point in one of four directions in the plane of the surface: $\rightarrow$, $\leftarrow$, $\uparrow$ or $\downarrow$. Calculate and compare the multiplicity for two "cases": a) we first place N identical particles on the lattice, then we assume that each dipole moment can point in any direction; b) we have $N/4$ particles with each dipole moment that are placed on the lattice [Hint: use Stirling's formula, $\ln N! = N \ln N - N$, that is valid for large N.]